Inorg. Chem. **1984**, *23*, 4297–4302 **4297**

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Crystal and Molecular Structure of Sodium Pentacyanonitrosylruthenate(II) Dihydrate and Its Spectroscopic Properties and Reactivity[1]

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Received October 12, 1983

The compound $Na_2Ru(CN)_5NO\cdot 2H_2O$ has been synthesized from ruthenium trichloride and sodium cyanide by oxidation with nitric acid. The orange prismatic crystals belong to the orthorhombic space group *Pnmm* with a = 6.303 (2) Å, b = 12.084 (4) Å, c = 15.833 (5) Å, and Z = 4. The structure was refined with use of the initial atomic coordinates from the isostructural sodium nitroprusside, $Na_2Fe(CN)_5NO\cdot 2H_2O$, to R = 0.030, R_w = 0.028, for 1588 independent reflections; hydrogen atoms were then located in a difference Fourier synthesis and refined with use of constraints in bond lengths (R = 0.024, R_w = 0.023). Important bond lengths and angles are as follows: Ru–N = 1.773 (3) Å, N–O = 1.130 (4) Å, Ru–C(trans) = 2.051 (4) Å, Ru–C(cis) = 2.053 (3), 2.064 (3) Å, C–N(trans) = 1.136 (5) Å, C–N(cis) = 1.145 (4), 1.149 (4) Å, ∠RuNO = 174.4 (3)°. The structure, together with data from infrared and electronic absorption spectra, is discussed in terms of π-acceptor and π-donor capabilities of the ligands and the Ru central atom, respectively. The electrophilic reactivity of the anionic complex has also been studied by its reaction with OH^-, SH^-, SO_3^{2-}, NH_3, and N_2H_4. They form addition intermediates, which further decay to generate final products, one of them presumably $Ru(CN)_5H_2O^{3-}$, an important precursor to other related $Ru(CN)_5X^{n-}$ complexes.

Introduction

The structural chemistry of metal nitrosyls is a matter of current interest and has been recently reviewed.[3] In the general class of mononitrosyl, six-coordinated complexes of formula $\{ML_5NO\}^6$ (the superscript is the number of electrons associated with the metal d orbitals and the π^*(NO) orbitals),[3] the group of substances for which L = CN^- and M is a metal from the first transition period has been thoroughly studied. This is not the case for metals from the second and third series. For M = Ru, the potassium salt was prepared many years ago,[4] and some spectroscopic (IR, electronic,[5] and Mössbauer[6]) properties were measured, as was done in part with the lithium salt.[7]

No structural data exist however for salts containing the pentacyanonitrosylruthenate anion. This is presumably due to the striking insolubility of the potassium compound. We have now succeeded in preparing the sodium derivative, which crystallizes as a dihydrate. A single-crystal structural analysis has been done and will be reported here, together with the measurement of spectral (IR, electronic) properties. Some photochemical results and a general reactivity pattern of coordinated NO toward different nucleophilic reagents are also presented.

Although the general structural properties of six-coordinated $\{MNO\}^6$ complexes are well delineated,[3] the inclusion of the cyanide complex in the $\{RuL_5NO\}$ series (complete structural work exists only for L = NH_3[8] and Cl^-[9]) provides a good opportunity for looking at finer details on the influence of the NO ligand on the other L bonding properties, as has been shown to occur with different cis- and trans-Ru–Cl distances in $RuCl_5NO^{2-}$.[9]

As the sodium salt is quite soluble, a rich chemistry associated with the nucleophilic attack on coordinated NO can also be developed;[10] in this context, new synthetic routes to the generation of $Ru(CN)_5X^{n-}$ are thus opened, X spanning a broad range of ligands with different bonding properties.[11,12]

Experimental Section

Synthesis of the Complex. A conventional method previously used for the sodium nitroprusside synthesis was adapted for our purpose.[13] In a typical experiment, an aqueous solution (25 mL) of ruthenium trichloride (0.2 g, Johnson Matthey) was heated at ca. 70 °C while sodium cyanide was added in successive amounts until the color changed from violet, blue, and then green to a final pale yellow (ca. 5 g). Then, NO_3H (38%, 50 mL) was added; the nitrosation process was carried out during 5–6 h, by heating in a water bath with periodical shaking. The solution attained a red brownish color; it was left overnight and then was neutralized with Na_2CO_3 (pH 7) and further heated in the bath for concentration; after successive separations of a large excess of $NaNO_3$ and reduction of the volume to about 3–4 mL, a small quantity of orange prismatic crystals could be picked up and separated from $NaNO_3$ crystals; this procedure was repeated for the smaller volumes of remaining solution, but a yield higher than 5% could never be attained for the pure compound. This was however sufficient for our present purposes. Analytical results for sodium (flame photometry) and water content (thermal gravimetry) conformed to the proposed formula.

Spectral Measurements. IR spectra were recorded on a Perkin-Elmer 580B spectrophotometer (4000–200 cm^{-1}; Nujol mull, CsI windows). Electronic absorption spectra in the range from 600 to 200 nm, as well as conventional kinetic measurements, were performed on a Shimadzu UV-210A double-beam spectrophotometer.

Collection of *X*-ray Diffraction Data. The space group and approximate unit cell parameters were determined from Weissenberg photographs using Cu Kα radiation. Systematic absences $0kl$, $k + l = 2n$, and $h0l$, $l + h = 2n$, were consistent with the space group *Pnnm*. Comparison of unit cell parameters and systematic absences indicated that $Na_2Ru(CN)_5NO\cdot 2H_2O$ is isostructural with the corresponding Fe compound. A crystal of approximate dimensions 0.30 × 0.15 × 0.10 mm was used for the determination of accurate unit cell parameters and collection of intensity data. The cell parameters and orientation matrix were determined by least squares from the

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(1) Part of the present work was presented at the Reunión Nacional de Física, Dec 1982, La Plata, Argentina, and at the III Congreso Argentino de Fisicoquímica, Sept 1983, La Plata, Argentina.

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Table I. Summary of Crystal Data and Intensity Collection

color of the cryst: pale orange
habit: prismatic plates
space group: *Pnnm*, $Z = 4$
$a = 6.303$ (2) Å; $b = 12.084$ (4) Å; $c = 15.833$ (5) Å
$V = 1206$ Å^3
$\rho_{\text{calcd}} = 1.890$ Mg m^{-3}; $\rho_{\text{obsd}} = 1.850$ Mg m^{-3} [a]
temp: 298 K
$F(000)$: 644
radiation: Mo Kα, graphite monochromator
linear abs coeff: 12.35 cm^{-1}
scan type: $\omega/2\theta$
scan width: $(1 + 0.34 \tan \theta)°$
aperture: $(1.4 + 0.8 \tan \theta)$ mm
max scan time: 60 s
2θ limits: 3.0–60.0°
octants collected: $(h, \pm k, \pm l)$
range of transmission factors: 0.691–0.827
total reflcns collected: 7452
criterion for observn: $I > 2\sigma(I)$
unique data: 1588
$R = 0.024$
$R_w = 0.023$
ratio of max LS shift to error: 0.068
av ratio of shift to error: 0.0003
max, min height in final diff Fourier: 0.77, −0.92 e Å^{-3}

[a] Value obtained by flotation in tetrabromoethane–CCl_4 solution.

Table II. Final Positional Parameters (× 10^4) for $Na_2Ru(CN)_5NO \cdot 2H_2O$[a]

atom	x	y	z
Ru	4994 (1)	2809 (0)	5000 (0)
N(4)	7331 (6)	3624 (3)	5000 (0)
O(1)	8911 (6)	4067 (3)	5000 (0)
C(1)	2397 (7)	1786 (3)	5000 (0)
N(1)	960 (7)	1218 (4)	5000 (0)
C(2)	6123 (4)	1761 (2)	5917 (2)
N(2)	6693 (5)	1171 (2)	6436 (2)
C(3)	3388 (5)	3670 (2)	4074 (2)
N(3)	2450 (5)	4096 (3)	3543 (2)
Na(1)	5000 (0)	0 (0)	2464 (1)
Na(2)	0 (0)	0 (0)	3770 (1)
O(2)	1729 (5)	1231 (2)	2699 (2)
H(1)	1790 (112)	1990 (20)	2870 (48)
H(2)	621 (66)	1176 (48)	2287 (29)

[a] In this table and those subsequent, estimated standard deviations in the least significant figure are given in parentheses.

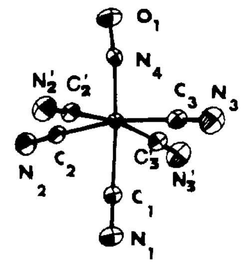

Figure 1. Geometry of the $Ru(CN)_5NO^{2-}$ anion.

Table III. Bond Angles (deg) and Bond Lengths (Å) within the Pentacyanonitrosylruthenate(II) Anion

	Angles		
Ru-N(4)-O(1)	174.4 (3)	C(2)-Ru-C(2′)	90.0 (2)
Ru-C(1)-N(1)	179.9 (1)	C(2)-Ru-C(3)	169.6 (1)
Ru-C(2)-N(2)	178.0 (3)	C(2)-Ru-C(3′)	88.7 (3)
Ru-C(3)-N(3)	176.3 (3)	C(3)-Ru-C(3′)	90.6 (2)
C(1)-Ru-N(4)	176.7 (2)	N(4)-Ru-C(2)	93.1 (1)
C(1)-Ru-C(2)	84.6 (1)	N(4)-Ru-C(3)	97.3 (1)
C(1)-Ru-C(3)	85.0 (1)		
	Lengths		
Ru-C(1)	2.051 (4)	C(1)-N(1)	1.136 (5)
Ru-C(2)	2.053 (3)	C(2)-N(2)	1.145 (4)
Ru-C(3)	2.064 (3)	C(3)-N(3)	1.149 (4)
Ru-N(4)	1.773 (3)	N(4)-O(1)	1.130 (4)

setting angles of 15 reflections, having $2\theta > 60°$, measured on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation. A summary of the crystal data and intensity data collection is given in Table I. The three standard reflections $\bar{2}\bar{5}1$, $\bar{2}\bar{2}\bar{6}$, and 210 were periodically measured as a check of crystal and electronic stability, without significant change. Intensity data were corrected for Lorentz, polarization, and absorption effects.

Solution and Refinement of the Crystal Structure. The initial atomic coordinates were taken from the structure of the iron complex.[14] The structure was refined by the method of full-matrix least squares and F magnitudes, with about 13 data per independent parameter.[15] The atomic scattering factors for Ru(III) and Na^+ were taken from ref 16 and 17, respectively. The positional parameters were refined along with isotropic thermal parameters to an R of 0.047. Anisotropic refinement for all non-hydrogen atoms led to reliability indices of $R = 0.030$ and $R_w = 0.028$ (where $R_w = \sum w^{1/2}(F_o - F_c)/\sum w^{1/2}F_o$). The weighting scheme used was $w = 6.9/\sigma^2(F) + 0.000078F^2$). At this stage, hydrogen atoms were located in a further difference Fourier synthesis and then positional and isotropic thermal parameters allowed to refine with use of a constraints in O–H bond lengths (0.96 ± 0.01 Å). Final R and R_w values obtained were 0.024 and 0.023, respectively. The largest peak in the last difference Fourier map having an electron density of 0.77 e Å^{-3} occurred near the Ru atom. The final atomic coordinates with esd's are given in Table II and the supplementary material.

Results and Discussion

Description of the Structure. The structure consists of a packing of layers of anions, linked by sodium cations and water molecules (supplementary material), as was found in the isostructural iron compound.[14] The geometry of the anion is shown in Figure 1. Bond distances and angles within the anion are shown in Table III. The coordination polyhedron around ruthenium is a slightly distorted octahedron with crystallographically imposed C_s symmetry, the mirror plane bisecting the N(2)–Ru–N(2′) and N(3)–Ru–N(3′) angles. The only significant deviation from idealized C_{4v} symmetry is the Ru–N–O angle of 174.5 (4)°. The maximum deviation from the two vertical planes corresponding to the idealized C_{4v} symmetry and containing the C and N atoms is that one displayed by the O atom of the NO (0.075 (3) Å); these two vertical planes make an angle of 91.6° with one another. The displacement of the Ru atom out of the plane of the cis C and toward the NO group (0.188 (1) Å) is responsible for the angle C(2)–Ru–C(3) of 169.5 (1)°.

The above-mentioned picture is consistent with an almost linear Ru(II)–N–O bonding scheme, typical for NO^+ coordinating to a d^6 metal center. Both the Ru–N distance (1.776 (5) Å) and the N–O distance (1.130 (4) Å) also indicate a multiple character of the Ru–N–O bond.[3,18]

The length of the trans- and cis-Ru–C bonds are equal within experimental error, and a slight tendency to longer distances is observed for the cis-C–N bond. On the grounds of structural data obtained for $RuCl_5NO^{2-}$,[9] the significant trans shortening of the Ru–Cl bond was interpreted as arising from strongly unequal σ–π interactions produced by Cl^- and NO^+ ligands. In the case of our complex, also with consideration of σ effects, a trans shortening of the Ru–C bond

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Table IV. Hydrogen-Bond Distances and Angles[a]

O_W–H···A	H···A, Å	O_W···A, Å	O_W–H···A, deg
O(i/2)–H(i/2)···N(ii/3) (N*4B*)[b]	2.399 (56)	3.344 (4)	169.0 (3.2)
O(i/2)–H(i/1)···N(i/3) (N*4D*)[b]	2.791 (43)	3.729 (9)	171.1 (2.8)
O(i/2)–H(i/1)···N(iii/2) (N*3E*)[b]	3.178 (35)	3.722 (7)	117.9 (3.0)

[a] cf. Figure 2. The water molecule was refined as a rigid body. [b] Nomenclature adopted by Holzbecher et al.[21] Symmetry code: (i) x, y, z; (ii) $-0.5 + x, 0.5 - y, 0.5 - z$; (iii) $-0.5 + x, 0.5 - y, -0.5 + z$.

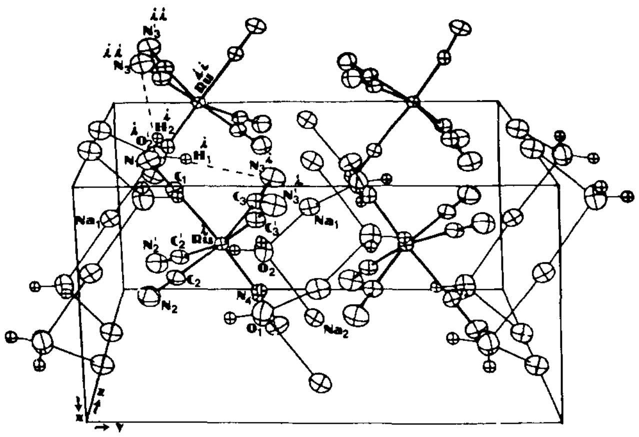

Figure 2. Thermal ellipsoids, oxygen–sodium interactions, and hydrogen-bonding scheme in the unit cell of $Na_2Ru(CN)_5NO.2H_2O$. Arbitrary radii have been taken for hydrogen atoms for the sake of clarity.

should thus be expected, as cyanide is known to be a good σ donor compared to the much weaker NO^+.[19] However, the strong d_{xz},d_{yz}(Ru) + π^*(NO) interaction would expectedly weaken the trans-Ru–C bond compared to the cis Ru–C, as trans cyanide does effectively compete with NO^+ for the same Ru orbitals; A compensating effect seems to be operative and would thus account for our experimental result. It is quite interesting to check the above reasoning when analyzing the observed relative shortening of the trans-C–N bond; in this case, the higher σ-donor and lower π-acceptor bonding properties of trans C–N both contribute to the relative strengthening of the C–N bond, as electron density changes are associated with antibonding orbitals in either case.[19] In contrast, no changes in Fe–C or C–N distances were found for the analogous iron complex, [FeNO], probably because the magnitude of the differential effect on C–N distances is of the same order as experimental uncertainties.

The coordination polyhedra around the sodium atoms are slightly distorted octahedra. Water molecules are weakly bound to N atoms of CN groups. No hydrogen bonding to NO^+ is observed; as weak hydrogen bonding is essentially electrostatic,[20] this should be a general feature of complexes containing positively charged NO groups. A possible hydrogen-bonding scheme is shown in Table IV, where the nomenclature given by Holzbecher et al.[21] for [FeNO] is included for comparison. N*4B* (N(ii/3) is confirmed as the acceptor to H(1);[21] N*4D* (N(i/3)) is now unambiguously determined by both the H···acceptor distances and O_w···acceptor angle (see Table IV). *The proposed hydrogen-bonding scheme is shown* in Figure 2.

Infrared Spectrum. The general shape of the spectrum is coincident with that from [FeNO].[22] The data are displayed in Table V, together with those from the iron complex; detailed vibrational measurements[22,23] with the latter substance allow us to make our assignments in a rather straightforward manner.

Table V. Wavenumbers (cm^{-1}) and Assignments in the Infrared Spectra of $Na_2M(CN)_5NO{\cdot}2H_2O$ (M = Ru, Fe)

Ru	assignt[a]	Fe[a]
3847 m	2 ν(NO)	3870
3633 m	ν_3(OH)	3627
3551 m	ν_1(OH)	3546
2184.0 m	ν(CN) A_1(ax)	2173
2173.5 m	ν(CN) A_1(eq)	2160
2165.5 m	ν(CN) B_1(eq)	2156
2151.0 s	ν(CN) E(eq)	2143
1926.0 s	ν(NO)	1945
1623 sh	δ(HOH)	1624
1617 m		1618
1612 sh		1612
645 m	ν(MNO) E	666.5
585 m	ν(MN) A_1	656.8
512 m, br	L (H_2O)	519
460 w	ν(MC) A_1(ax)	468
422 sh	ν(MC) E(eq)	433
410 s		424
400 s	ν^{θ}(MCN) E	417
350 m, br	L (H_2O)	342
310 m	ν^{λ}(MCN) E	321.5

[a] Assignments and data from ref 28.

(a) Nitrosyl Stretching Vibration. The wavenumber for ν(NO) is known to be highly sensitive to the nature of M and L in the $\{ML_5NO\}$ series.[24] Significant changes have also been detected depending on either the type of countercation or the presence of water molecules when data for several pentacyanonitrosyliron complexes are compared.[24] All other factors being equal, assuming that the M(II)–NO^+ interaction is mainly governed by π effects and the σ contribution is negligible or at least essentially constant,[19] we can interpret the lower number for ν(NO) in [RuNO] as arising from the higher π-donor capability of Ru(II) when compared to that of Fe(II). This problem has already been discussed elsewhere,[25] including vibrational[26] and Mössbauer[7] spectral data from several hexacyanides and pentacyano-L-metalates. On the other hand, the influence of maximum competitive π-acceptor effects in the presence of cyanide is evident by the highest ν(NO) value found for the cyanide complex, when the $\{RuL_5NO\}$ series is considered. ν(NO) is found at 1916 cm^{-1} for L = Cl^{-3} and at 1903 cm^{-1} for L = NH_3.[27] Even lower ν(NO) values are found for $Na_2Ru(NO)(NO_2)_4(OH)$, 1893 cm^{-1}, and for $Ru(NO)(NH_3)_4(OH)Cl_2$, 1834 cm^{-1}.[27]

(b) Cyanide Stretching Vibrations. Our complex shows the same four-component pattern for ν(CN) as found in [FeNO];[22] although only three modes (2 A_1 + E) should be IR active for the isolated anion in C_{4v} symmetry, activation of the B_1 mode has already been interpreted as arising from coupling with the E mode.[28] ν(CN) values in [FeNO] are considerably high, if we compare them with those found in iron(II) hexacyanides and other iron(II) pentacyanides.[29] The changes reflect the

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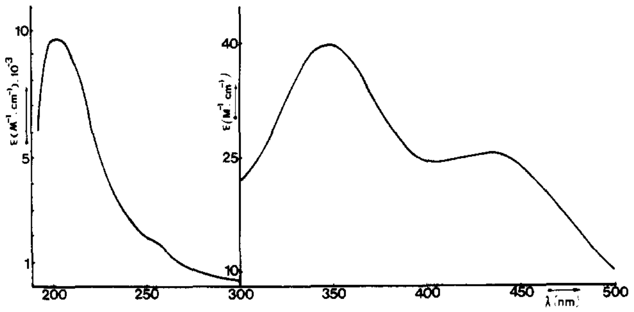

Figure 3. Electronic spectra of $Na_2Ru(CN)_5NO \cdot 2H_2O$ in aqueous solution (left curve) UV spectrum of 1.6×10^{-4} M solution; (right curve) visible–near-UV spectrum of 1.6×10^{-2} M solution (1-cm path length).

depletion in σ- and π-orbital populations from cyanide ligands when going from $M(CN)_6^{n-}$ to $M(CN)_5NO^{n'-}$, as a result of the flow of electrons to NO^+. As both σ, π orbitals are antibonding in character, the result is a strengthening of the C–N bond and thus a higher ν(CN). An orbital occupation analysis showed[19] that the relative changes thus occurring in the π orbitals from CN^- were more significant than the related ones corresponding to the σ orbitals. In this context, the higher wavenumbers for ν(CN) in [RuNO] compared to those for [FeNO] are reasonably interpreted as a consequence of the greater π acceptance by NO^+ in the first complex (see above), with concomitant changes in cyanide orbital populations, in the above-mentioned sense. As a result of these electronic interactions, a lower tendency to the formation of hydrogen bonds through the nitrogen end of cyanide is anticipated for [RuNO].

(c) Metal–Ligand Stretchings and Deformations. A general tendency to lower wavenumbers is found in [RuNO] compared to [FeNO], those values in probably due to the influence of mass effects. A noticeable difference in the Ru–C axial and equatorial stretchings is found again, as with [FeNO]. As no substantial differences in the corresponding Ru–C distances were found, a coupling of the axial mode with the Ru–N stretching mode is probably operating. The wavenumber for the Ru–N stretching, ν(Ru–N), is noticeably low compared to ν(Fe–N); the higher π contribution should act in the opposite sense, and therefore a greater influence of the mass effect is perhaps operative in determining ν(M–N) values. Our assignment is also supported by available data on related $\{RuNO\}^6$ complexes.[27,30] Remarkably, the lowest value for ν(Ru–N) is found for [RuNO], which reflects the π-withdrawing effects from CN^-, thus resulting in a relative weakening of the Ru–N bond.

(d) Water Vibrations. Both ν(OH) values occur at higher wavenumbers in [RuNO], suggesting weaker hydrogen-bond interactions compared to those in [FeNO]. As shown above, this relates to the differences in electron-withdrawing effects from the respective M–NO moieties. A lower electron density and, consequently, a lower acceptor strength are associated with the N end of cyanide in [RuNO].[31] $\delta(H_2O)$ values are split into three components, as in [FeNO]; a factor group analysis indicates that each internal vibration should produce eight corresponding modes of the unit cell. Only three of them, B_{1u}, B_{2u}, and B_{3u}, are IR active.[21] Librational modes (broad bands at 512 and 350 cm^{-1}) are also assigned from analogy to [FeNO].

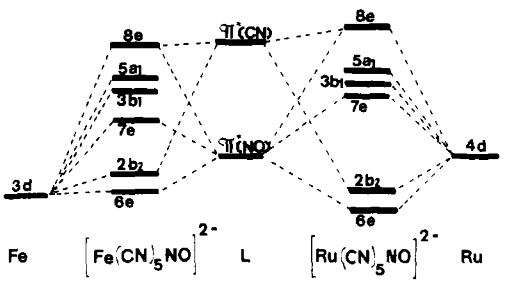

Figure 4. Simplified qualitative MO diagram for $M(CN)_5NO^{2-}$ (M = Fe, Ru). Metal s and p and ligand σ and π contributions to MO levels have been omitted for clarity.

Table VI. Electronic Spectral Data and Assignments

$Fe(CN)_5NO^{2-}$ [a]			$Ru(CN)_5NO^{2-}$	
ν, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	band assignts[b]	ν, cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}
20 080	8	$2b_2(xy) \rightarrow 7e$	22 988	26
25 380	25	$6e(xz,yz) \rightarrow 7e$	28 985	39
30 300	40	$2b_2(xy) \rightarrow 3b_1(x^2-y^2)$	39 215	1550[c]
37 800	900	$6e(xz,yz) \rightarrow 5a_1(z^2)$		
42 000	700	$6e(xz,yz) \rightarrow 3b_1(x^2-y^2)$		
50 000	24000	$2b_2(xy) \rightarrow 8e$	50 000	9400

[a] Data from ref 32. [b] cf. ref 32. [c] Without background.

Electronic Spectrum. The measured spectrum in the visible–UV region is shown in Figure 3. The assignment of electronic transitions is based on the model of Manoharan and Gray for pentacyanonitrosylmetalates.[32] A simplified MO energy level diagram is displayed in Figure 4; the spectral data and their proposed assignments are shown in Table VI.[33]

As suggested by energetic and overlap considerations, we are assuming a more favorable interaction between 4d orbitals from ruthenium and π*(NO) orbitals, compared to that occurring in [FeNO]; as a result, a greater relative stabilization of the 6e orbitals and a corresponding destabilization of the 7e (mainly π*(NO)) orbitals is expected in [RuNO]. As shown by a population analysis, the 6e level is 24.8% π*(NO) in [FeNO], indicating substantial back-bonding.[32] This is effectively shown to increase in [RuNO], as measured by its lower ν(NO). Thus, the first two low-energy bands might be assigned to charge-transfer transitions of metal-to-ligand type; both are blue shifted compared to corresponding transitions in [FeNO]. The shift of the second band ($\Delta\nu_{Ru-Fe}$ = 3605 cm^{-1}) is higher than that for the first transition ($\Delta\nu_{Ru-Fe}$ = 2908 cm^{-1}). This is consistent with an approximately nonbonding character of the $2b_2(xy)$ level, compared to the strongly stabilized $6e(xz,yz)$.[32,34]

The above assignments are partly supported by available data on related transitions for several iron and ruthenium compounds; i.e., the intervalence band found in the Prussian blue analogues is shifted 3300 cm^{-1} toward higher energies in $(Ru(CN)_6)_3Fe_4$ compared to that in $(Fe(CN)_6)_3Fe_4$.[35] Similarly, a shift of ca. 2630 cm^{-1} in the same direction was

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(29) Tosi, L.; Danon, J. *Inorg. Chem.* **1964**, *3*, 150.

(30) Miki, E.; Mizumachi, K.; Ishimori, T.; Okuno, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3779.

(31) However, hydrogen bond lengths and angles calculated from hydrogen positions reported for [FeNO][14] are not in agreement with our IR observations; on the other hand, a theoretical refinement performed on the hydrogen positions for [FeNO] (Rigotti, G.; Alzari, P. M.; Varetti, E. L.; Aymonino, P. J., work in progress) leads to slightly stronger hydrogen bonds for the latter compound, as expected; therefore, it is suspected that the X-ray hydrogen positions given for [FeNO] are not realistic. This view is also supported because of the short O–H and H–H distances and the rather small H–O–H angle involved.

(32) Manoharan, P. T.; Gray, H. B. *Inorg. Chem.* **1966**, *5*, 823.

(33) Data for lithium pentacyanonitrosylruthenate have been published;[7] the spectrum is different, with slight changes in the low-energy bands. This should not be unexpected, probably due to the quite different polarizing properties of Li^+, Na^+ countercations.

(34) Bottomley, F.; Grein, F. *J. Chem. Soc., Dalton Trans.* **1980**, 1359. A significant contribution from π-donor CN^- orbitals has been proposed when analyzing the nature of the HOMO in [FeNO].

(35) Robin, M. B. *Inorg. Chem.* **1961**, *1*, 337.

found in comparing the centers of gravity of the high-energy M → π^*(CN) transitions in hexacyanometalates (Fe, Ru).[36]

The energy of these bands ($2b_2$,6e → 7e) should be dependent on the nature of other coordinating ligands, as was shown in the series of $Ru(NH_3)_4(NO)L^{n+}$ (L = Cl^-, OH^-, NH_3, etc.).[37] Our results can be compared with available data for $\{RuL_5NO\}$ complexes: both bands are shifted to lower energies as one goes from L = CN^- (435, 345 nm) to L = NH_3 (474, 417 nm) and L = Cl^- (568, 510 nm).[7] The results are consistent with a relative destabilization of metal orbitals when the character of the π interaction changes from a strongly acceptor type of ligand (CN^-) to a π-donor type (Cl^-), the case of NH_3 being intermediate (no π interactions).

The shoulder at ca. 250 nm is presently assigned to a spin-allowed d–d transition; we cannot however assign it to a particular type of transition, as was done with $Fe(CN)_5NO^{2-}$ (cf. Table VI). Similar shoulders at the same wavelength have also been measured for the $Ru(CN)_5NH_3^{3-}$ and $Ru(CN)_6^{4-}$ anions, showing that there is not apparently any influence of the bonding type of L on the position of the d–d band in the $Ru(CN)_5L^{n-}$ series;[38] this is contrasting with previous results with the $Fe(CN)_5L^{n-}$ series.[39] On the other hand, the previous assignment of the 250-nm shoulder (which corresponds to the $^1A_1 \rightarrow {}^1T_1$ transition in $Ru(CN)_6^{4-}$) leads to a more reasonable value of Δ for the hexacyanoruthenate(II) ion, compared to Δ for the hexacyanoferrate(II) ion,[40,41] as has been recently discussed.[38] Besides, the blue shift of the d–d band in Ru(II) cyanide complexes compared to that band in Fe(II) related complexes is also consistent with the similar shift previously discussed for the charge-transfer bands (see above), as a result of the greater relative stabilization of the Ru(II) π-bonding orbitals. Finally, the intense band at 200 nm is most likely the $2b_2$ → 8e (mainly π^*(CN)) transition; a similar band has also been measured in [FeNO].[32]

It should be pointed out, however, that the assignments commented on above remain controversial, particularly when the identification of the excited state for the low- and medium-energy transitions is considered (cf. ref 18, 34 and references therein).

Photolysis Studies. The cyanonitrosyliron complex is photochemically active when exposed to broad-band (UV-filtered) diffuse daylight. On the other hand, the ruthenium complex shows no detectable chemical change under the same conditions. No reaction occurs even after irradiating with a medium-pressure Hg lamp (Airam, 125 W, $\lambda > 340$ nm) for 12 h. the photolysis of [FeNO], which generates $Fe(CN)_5H_2O^{2-}$ and NO as primary products, was interpreted as an excitation of the electron from a predominantly metal-localized bonding orbital (6e) to an orbital (7e) primarily centered on the nitrosyl ligand, thus resulting in a loss of strength of the Fe–N bond, followed by bond cleavage.[42] If the electronic spectral assignments are correct, a similar photooxidation reaction should be expected at the Ru center, as the operative charge-transfer transition is located at 345 nm.

A detailed work with $Ru(NH_3)_5L^{n+}$ (L = pyridine and derivatives)[41] showed that no photooxidation of Ru(II) to Ru(III) occurs as a result of irradiation of the M → L band; instead, photoaquation products were detected, and it was proposed that an interconversion from the charge-transfer state to a ligand field triplet state was operative. Photooxidation occurs however with high-intensity broad-band UV irradiation in these complexes;[43,44] the same was also observed when $Ru(bpy)_2(NO)Cl^{2+}$ was photolyzed with a medium-pressure lamp at 312 nm, although the interpretation of these results was not investigated in detail.[45]

A complete photochemical study is out of the scope of the present work; it is probable however that the noticeable differences found for both Fe and Ru cyano nitrosyl complexes are associated with greater spin–orbit coupling effects for Ru, as well as with a lower lability of the Ru(III) species in the excited state, compared to that of Fe(III). Both of these effects should act in the sense of the Ru complex affording preferentially a deactivation process through interconversion and vibrational relaxation mechanisms.[44]

Reactivity of Coordinated NO^+. The reactions of the pentacyanonitrosylruthenate anion with OH^-, SH^-, and SO_3^{2-} are similar to those found for the nitroprusside anion.[46] Intense absorption bands (325, 430, and 320 nm, respectively) are observed initially, which slowly decay to generate a final absorption band at ca. 285 nm. This is a common feature for all the reactions. The maxima of these Ru(II) intermediates are in all cases shifted to higher energies compared to those of analogous iron species. On the other hand, the reactions with N-coordinating nucleophiles such as hydrazine and concentrated ammonia are rapid processes that lead to the evolution of gaseous products, together with the formation of the same final band at 285 nm. The overall picture implies the general equation

$$Ru(CN)_5NO^{2-} + L \rightarrow \{Ru(CN)_5NO{\cdot}L\}^{n-} \rightarrow X_{285} + \text{products} \quad (1)$$

We have identified the band at 325 nm in the reaction with L = OH^- as corresponding to $Ru(CN)_5NO_2^{4-}$ (ϵ remains constant in the presence of free nitrite ion). Kinetic measurements show that the reaction is first order for both reagents, with $k = 3.2$ M^{-1} s^{-1} ($T = 25$ °C, $I = 1$ M). This is similar to the reaction of OH^- with [FeNO][47] (our number for k is, however, higher by a factor of 6). As was pointed out by Bottomley,[10] addition reactions occurs with coordinated NO^+ having as low an electron density as possible. A correlation of ν(NO) with electrophilic reactivity was thus shown to hold for a broad range of complexes spanning ν(NO) values from 1860 to about 2000 cm^{-1}. However, the observed higher reactivity of [RuNO] toward OH^- works in the opposite sense, as ν(NO) is effectively lower in the ruthenium complex. A systematic thermodynamic and kinetic approach to these reactions is now in progress.

Concerning the identity of the final product of reaction 1, X_{285}, the above-mentioned similarity of the reactions with OH^- for both nitrosyl complexes strongly suggests that X_{285} is $Ru(CN)_5H_2O^{3-}$. Moreover, its reactivity toward pyrazine, pyridine, and their derivatives leads to the formation of colored complexes, as expected from the well-known reactivity pattern of related $Ru(NH_3)_5H_2O^{2+}$ and $Fe(CN)_5H_2O^{3-}$.[48-50] A preliminary kinetic study shows in fact that a second-order process is operative for both X_{285} and $Ru(NH_3)_5H_2O^{2+}$ re-

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(48) A different approach to the generation of the $Ru(CN)_5H_2O^{3-}$ ion has recently been reported;[12] in that work, the aquo ion is claimed to absorb at 310 nm and also leads to $Ru(CN)_5pz^{3-}$ (pz = pyrazine), as well as to other related complexes, when reacting with the appropriate reagents.

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acting with pyrazine, with a value of the rate constant that is of the same order in both cases, thus reflecting a minor effect of the auxiliary ligands (NH_3 vs. CN^-) on the substitutional reactivity of the $Ru-OH_2$ bond.[11,49]

Conclusions

The iron and ruthenium pentacyanonitrosyl salts of sodium constitute a unique pair of substances where the comparative π-donor capabilities of both metal centers can be successfully assessed; this is favored by the analogous environment around the metals, as well as by the dominant character of the M(II)(d_{xz},d_{yz})–π^*(NO) interaction in the overall bonding scheme, the $\sigma(NO^+)$ contribution remaining negligible or at least essentially constant.

The consequences of the higher π-donor ability of Ru are reflected in the changes found in all of the measured fundamental vibrations in both complexes, including even the O–H stretchings of weakly hydrogen-bonded water molecules. The energy of electronic transitions are also strongly influenced by this phenomenon.

The most significant structural result that can be reasonably ascribed to the same origin is the relative shortening of the trans-C–N distance, a feature that could not be put in evidence in [FeNO]. A similar line of reasoning explains the equality of cis- and trans-Ru–C distances, as a result of self-compensating contributions. Thus, the cyanonitrosylruthenium complex behaves differently compared to $RuCl_5NO^{2-}$, as expected from the bonding properties of the ligands involved.

The competition of cyanide for the π-electron density also places [RuNO] in one of the extremes of a series of related $\{RuNO\}^6$ complexes, thus showing a tendency for weaker Ru–N bonds (higher Ru–N distance and lower ν(Ru–N)) and stronger N–O bonds (lower N–O distance[51] and higher ν(NO)).[3,18]

Finally, although the general reactivity picture is indeed common to both [RuNO] and [FeNO], a direct correlation between ν(NO) and electrophilic reactivity toward OH^- seems not to be operative in a strictly quantitative way; more detailed work will be performed in order to assess the influence of other possible factors, as well as to expand the studies to other nucleophiles. On the other hand, several evidences point to the common final product of these addition reactions to be $Ru(CN)_5H_2O^{3-}$, a result that allows for fruitful developments in the comparative chemistry of Ru(II) complexes.

Acknowledgment. This work was, in part, supported by the Comisiõn de Investigaciones Cientificas (Prov. Buenos Aires) and Secretaria de Ciencia y Tẽcnica. Valuable comments from Prof. E. Diemann (University of Bielefeld) are also gratefully acknowledged.

Registry No. $Na_2Ru(CN)_5NO\cdot 2H_2O$, 92763-38-7; $Ru(CN)_5NO_2$, 40209-40-3; $Ru(CN)_5H_2O^{3-}$, 74009-27-1; OH^-, 14280-30-9; SH^-, 15035-72-0; SO_3^{2-}, 14265-45-3; ammonia, 7664-41-7; hydrazine, 302-01-2.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters, positional and equivalent isotropic thermal parameters, and interatomic distances and bond angles within sodium polyhedra and a stereoscopic projection down *c* showing the packing of the structure (30 pages). Ordering information is given on any current masthead page.

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(51) However, comparisons between N–O and Ru–N distances for structurally related complexes should be made with caution, as changes are evidently of the order of experimental errors (cf. the strikingly low number found for the N–O distance in $RuCl_5NO^{2-}$, 1.112 (7) Å).[9]

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Syntheses and Molecular Structures of Related Six- and Eight-Coordinate Complexes: Tetrachloro(2,2′-bi-2-thiazine)zirconium(IV), Tetrachlorobis(2,2′-bi-2-thiazoline)zirconium(IV), and Bis(2,2′-bi-2-thiazoline)tetrakis(isothiocyanato)zirconium(IV)

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Received February 22, 1984

The crystal and molecular structures of the six-coordinate complex $ZrCl_4(C_8H_{12}N_2S_2)$ (**1**) and the eight-coordinate complexes $ZrCl_4(C_6H_8N_2S_2)_2\cdot 2CH_3CN$ (**2**) and $Zr(NCS)_4(C_6H_8N_2S_2)_2$ (**3**) have been determined from single-crystal X-ray diffraction data collected by the θ–2θ scan technique. Compound **1** crystal data: $P2_1/n$, a = 18.478 (4) Å, b = 10.930 (3) Å c = 16.656 (4) Å, β = 109.76 (2)°, Z = 8, ρ_{calcd} = 1.82 g/cm³, ρ_{obsd} = 1.80 g/cm³. Compound **2** crystal data: $C2/c$, a = 14.199 (8) Å, b = 14.933 (7) Å, c = 13.825 (7) Å, β = 112.34 (4)°, Z = 4, ρ_{calcd} = 1.62 g/cm³, ρ_{obsd} = 1.62 g/cm³. Compound **3** crystal data: $P2_1/c$, a = 15.161 (8) Å, b = 21.627 (8) Å, c = 16.350 (3) Å, β = 96.99 (3)°, Z = 8, ρ_{calcd} = 1.67 g/cm³, ρ_{obsd} = 1.68 g/cm³. All three structures were refined by full-matrix least squares to the residuals 0.069, 0.053, and 0.053, respectively. Comparison of the three structures reveals a great deal about the factors that influence the shape of the coordination polyhedron. The two bithiazoline complexes, **2** and **3**, have geometries intermediate between an ideal dodecahedron and an ideal square anitprism. The bithiazine ligand is too large to permit the formation of an eight-coordinate $ZrCl_4(L-L)_2$ complex; thus, compound **1** results. The Zr–N bond lengths follow the crowding effects with 2.300 (10) Å for **1**, 2.463 (10) Å for **2**, and 2.388 (15) Å for **3**.

Introduction

The monomeric complexes tetrachloro(2,2′-bi-2-thiazine)zirconium(IV), $ZrCl_4(C_8H_{14}N_2S_2)$, tetrachlorobis(2,2′bi-2-thiazoline)zirconium(IV), $ZrCl_4(C_6H_8N_2S_2)_2$, and bis(2,2′-bi-2-thiazoline)tetrakis(isothiocyanato)zirconium(IV), $Zr(NCS)_4(C_6H_8N_2S_2)_2$, have been prepared as part of a study of the coordination of 2,2′-bi-2-thiazine (btz) and 2,2′-bi-2-thiazoline (bt) in related complexes. Previous use of these heterocyclic dimers as ligands has established that they normally coordinate through the nitrogen atoms.[1-3] Few complexes have been synthesized with either ligand, and no single-crystal structural studies have been reported on any com-

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